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Publication number:

**0 398 201  
A1**

**EUROPEAN PATENT APPLICATION**

Application number: 90108988.8

Int. Cl.<sup>3</sup>: C23C 22/12, C23C 22/28

Date of filing: 12.05.90

Priority: 18.05.89 US 353983

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Date of publication of application:  
22.11.90 Bulletin 90/47

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Designated Contracting States:  
AT BE DE DK ES FR GB IT NL SE

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Compositions and processes for improved preparation of metals for cold forming.

Reactive lubrication of phosphated metal surfaces is improved by using a combination of (A) a complexing agent for the divalent metal cations that are displaced from the phosphated layer into the lubricating solution and (B) organic molecules having at least one ether or hydroxyl oxygen for each eight carbon atoms, along with the conventional soluble soap, in the solution used for reactive lubrication. Most preferably, EDTA or its salts are used as the complexing agent and polyethylene glycol as component (B), with the concentration of EDTA being adjusted as needed during the process to keep the concentration of total titratable metals in the lubricating solution below 0.05 % by weight, and the amount of polyethylene glycol being adjusted as needed to maintain the optimum viscosity of the lubricating solution and optimum ratios of reactive to unreacted lube coating weights and of reacted lube coating weight to conversion coating loss.

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## COMPOSITIONS AND PROCESSES FOR IMPROVED PREPARATION OF METALS FOR COLD FORMING

Field of the Invention

The present invention relates to compositions and methods for lubricating phosphated metal surfaces prior to drawing or other cold forming processes on the lubricated metal.

Statement of Related Art

It has been known for many years to prepare metals for cold forming by phosphating followed by lubrication with a soap or similar material. Generally, phosphating from solutions that contain zinc ions, and sometimes also contain calcium, nickel, manganese, copper, and/or other divalent metal ions, is preferred as the phosphating step. An aqueous solution of alkali metal soap, capable of reacting with zinc phosphate to produce a very favorable form of zinc stearate called "reacted lube" in situ on the surface, is generally preferred for the lubrication stage.

Initially, a simple solution of reactive soap in water provides very effective lubrication. The lubrication process, however, is known to cause dissolution of part of the phosphate coating. For this and possibly other reasons, divalent metal ions accumulate in the lubricating solution as the process proceeds and eventually cause the lubricating coatings formed to become unsatisfactory.

U. S. Patent 4,199,381 of Apr. 22, 1980 to Nuss et al. teaches that, when lubricating surfaces formed in phosphating baths containing divalent metal ions that are incorporated into the phosphate coating formed, the results can be improved by incorporating complexing agents for such divalent ions into the lubricating solutions. The following sections of the specification of the Nuss patent, in so far as they are consistent with the statements made explicitly herein, are hereby incorporated into this specification by reference: Column 1 line 10 to column 2 line 4; column 2 lines 33 - 49; and column 3 lines 6 - 11.

Complexing agents as taught by Nuss are highly effective in increasing the useful life of lubricating solutions and in promoting usefully high coating weights of lubricant, but prolonged use of these complexing agents eventually results in increased lubricating solution viscosity, increased dissolution of the phosphate coating into the lubricating solution, drying problems, reduced lubricant adhesion, and higher proportions of less desirable "unreacted" lubricant in the lubricant coating formed. It is an object of the present invention further to improve the processes and compositions described by Nuss in order to ameliorate these difficulties.

U. S. Patent 3,556,996 of Jan. 19, 1971 to Jones et al. teaches the use of surfactants, including condensates of alcohols with ethylene oxide, in lubricating solutions, along with sugar and/or polyethylene glycol as optional components.

Description of the Invention

In this description, except in the operating examples or where expressly stated to the contrary, all numbers describing amounts of materials or conditions of reaction or use are to be understood in all instances as modified by the word "about".

It has been found that large amounts of complexing agents can be harmful to the reactive lubrication process after phosphating, so that better results are obtained by observing an upper limit on the concentration of complexing agent present, the upper limit being connected with the amount of complexable, divalent cations introduced into the lubricating solution during use. It has also been found that the reactive lubrication process can be improved by using aqueous lubricating solutions that, in addition to soluble metallic soaps having aliphatic anions with 8 to 22 carbon atoms and hydrolysis resistant complexing agents as taught by Nuss, contain water soluble or dispersible organic compounds that are stable in solution or dispersion under normal conditions of applying lubricant to phosphated surfaces and that contain at least one hydroxyl or ether oxygen for each eight carbon atoms. This latter component is referred to briefly hereinafter as "OSOC" (for "oxygenated soluble organic compound"). In the definition of the OSOC component, neither oxygen atom of a carboxyl or carboxylate group is considered to be an ether or hydroxyl oxygen. Preferably, the OSOC component molecules contain at least one hydroxyl or ether oxygen for each two carbon atoms.

The water soluble soap to be used in this invention may be any material known for such a use in the

art, including technical sodium stearate containing from 40 to 80 % of C<sub>18</sub> soaps, as used in some examples of the Nuss patent noted above, but technical mixtures including a higher proportion of sodium stearate are generally most highly preferred. The complexing agent similarly may be any material known as such in the art, but preferably is selected from the group consisting of ethylene diaminetetraacetic acid (hereinafter "EDTA") and its salts, nitrilotriacetic acid (hereinafter "NTA") and its salts, N-hydroxyethyl-ethylene diaminetriacetic acid (hereinafter "NEDTA") and its salts, diethylene triamine pentaacetic acid and its salts, diethanol glycine, and a material having CAS Registry No. 68611-02-9 and described by its manufacturer as "glycine,N,N'-1,2-ethanediybis[N-carboxymethyl]-, reaction products with citric acid, D-gluconic acid, and triethanolamine, sodium salt." EDTA and its salts are most preferred.

The OSOC component is preferably selected from the group consisting of alkylene glycols, polyalkylene glycols, glycol ethers, ethoxylated alcohols, polymers and copolymers of ethylene oxide and propylene oxide, and glycerin.

For both the complexing agent and the OSOC component, mixtures of materials from the preferred group are equally as preferred as single chemical types of materials, unless otherwise noted.

Poly(ethylene glycol), hereinafter "PEG", is more preferred than other OSOC materials, with PEG having a molecular weight of about 4000, hereinafter "PEG 4000", being most preferred. When the OSOC component consists essentially of PEG 4000, it is preferred that the ratio of the concentration of the complexing agent to the concentration of the OSOC component lie within the range of 1 - 5, more preferably within the range of 2.5 to 3.5, and most preferably within the range of 2.9 - 3.1.

It is preferred that the concentration of reactive soap in the solutions according to the invention lie within the range of 5 to 150 g/L of solution. The preferable concentrations of complexing agent are determined by balancing several considerations, as noted further below.

A process embodiment of this invention may be performed by contacting a suitable phosphated surface with a lubricating solution according to the invention, as generally described above. It is believed that there is no advantage from the presence of the complexing agent in the very early stages of use of a freshly prepared lubricating solution, before any significant amounts of divalent metal ions have accumulated in the lubricating solution as a result of its exposure to a phosphated surface. However, it has been found that there is no apparent harm from an initial concentration of complexing agent as high as 0.1 gram per liter (hereinafter "g/L"), and the use of solutions initially made up to contain about this amount, or slightly less, of complexing agent is generally preferred in practice, in order to avoid the need to add complexing agent within a relatively short time after a fresh lubricating solution has been put into use.

An ideal lubricating process would maintain a consistent, high coating weight level of reacted lube, avoid the introduction into the lubricating solution of byproducts that interfere with the desired reaction between constituents of the phosphate coating and constituents of the lubricating solution, and remove little or none of the phosphate coating that was on the metal when it entered the lubricating solution. No actual lubricating solution known can accomplish such ideal lubrication, but preferable practical baths tend toward maximizing the ratio of reacted lube coating weight to conversion coating loss, with consideration toward optimizing the ratio of reacted lube coating weight to unreacted lube coating weight.

The most preferred embodiments of the process according to the invention utilize complexing agents and OSOC component in lubricating baths from near the beginning of use of a freshly made bath. In such embodiments, satisfactory operating conditions can generally be attained by selecting an upper bound on the concentration of "titratable metals", as defined exactly below, and by adding complexing agent after each measurement of titratable metals concentration that is higher than the selected upper limit. The amount of complexing agent should be at least sufficient to bring the concentration of titratable metals under a selected upper limit value. The best upper limit value may be determined most precisely from experience with each particular lubricating solution composition and type of base metal and phosphate coating lubricated, but in general an upper limit of 0.05 % by weight or less is preferred.

Most preferably, lubricating processes and solutions according to this invention should be controlled, from the beginning of use of a freshly made solution, so that the concentration of titratable metals never rises above its selected upper limit during the entire period of use of a lubricating solution according to the invention. Therefore, it is more preferable to add sufficient complexing agent, after each measurement of titratable metals, to bring the titratable metals concentration below two-thirds or less of its upper limit value immediately after addition, and to measure the titratable metals concentration sufficiently often so as to assure that the concentration never rises above the selected upper limit. It is generally most preferable in such situations to add sufficient complexing agent to bring the titratable metals concentration below 0.01 % by weight after each measurement of a higher value for this concentration.

While the method described above of utilizing lubricating solutions that contain complexing agent and OSOC components from at or near the beginning of their use is most preferred, the process according to

this invention may also be usefully embodied by starting with a conventional lubricating solution, containing little or no complexing agent, that has already been used for phosphating to a sufficient extent to accumulate a concentration of titratable metals greater than the desired upper limit for processes according to this invention. In such an embodiment, it has been found that it may be disadvantageous to add the very large amount of complexing agent that might be needed to reduce the concentration of titratable metals to very near zero. Such a large amount of complexing agent may cause excessive conversion coating losses during lubricating. Instead, when a process according to this invention is being initiated with a lubricating solution already containing more than 0.05 % by weight of titratable metals, it is preferable to add initially an amount of complexing agent that will produce a concentration of complexing agent in the solution that is within the range of 5 to 9 times the measured titratable metals concentration, with a ratio of 6.5 - 7.5 most preferred. At the same time, sufficient OSOC component to maintain the preferred ratio between the complexing agent and the OSOC component as stated above is also preferably added. The concentration of titratable metals remaining after this initial addition of complexing agent is then preferably measured; it will usually be between 0.01 and 0.05. After the initial addition of complexing agent, the process according to the invention is preferably continued in the same general manner as described above for embodiments in which complexing agent is added to the lubricating solution from the beginning of its use, except that the additions of complexing agent should be limited so that they do not reduce the concentration of titratable metals below three-quarters of their concentration after the initial addition of complexing agent.

In all processes according to this invention, the OSOC component preferably should be added to the lubricating solution at the same time as the complexing agent, in sufficient amount to maintain the ratio between these two components within the already stated preferred range.

After some operating experience with the same or a similar type of metal substrate and phosphating conditions, it is readily feasible to operate the process according to this invention successfully without explicitly measuring the concentrations of dissolved titratable metals, simply by adding appropriate amounts of complexing agent and OSOC components to a lubricating solution at intervals as the solution is used for lubricating.

The temperature of the lubricating solution and the time of contact between the lubricating solution and the phosphated surface in any process according to this invention are generally within the range of such conditions as used in the art for reactive lubrication. For example, the temperature is usually preferably between 70 and 90° C and the time of contact between 1 and 10 minutes.

The practice of the invention may be further appreciated with the help of the following non-limiting operating examples.

#### Examples

##### General Conditions for All the Examples and Comparative Examples

The temperature of the lubricating solutions was maintained at 79° C, and phosphated metal specimens were contacted with the solution for 5 minutes, then dried for 15 minutes in an oven maintained at 121° C. The test specimens were Type 1010 cold rolled steel that had been phosphated by use of Bonderite® 181x, a commercial zinc phosphating solution available from the Parker + Archem Division of Henkel Corporation, Madison Heights, Michigan, in a solution maintained with a total acid number of 30 points. (Points in this instance are defined as the number of milliliters of 0.1 N NaOH solution required to titrate a 5 ml sample of the phosphating solution to a phenolphthalein end point.) The average phosphate coating weight was 12.8 grams per square meter of surface (g/m<sup>2</sup>) for all the panels except those used in Experiment 5, for which the average coating weight was 21 g/m<sup>2</sup>.

The free acid or free alkalinity and the titratable metals content of the lubricating solutions were measured according to the following procedures:

##### Free Acid

Pour 200 ml of a solution of 0.2 % by weight phenolphthalein in isopropyl alcohol into a 400 ml beaker, then add a 10 ml sample of hot lubricating solution, measured with a conical graduate or a pipet. Heat the

5 mixture in the beaker to boiling, and boil for at least one minute. Remove from heat and titrate immediately, while the solution is still hot, with 0.1 N NaOH solution if the solution is clear rather than pink, to the development of a permanent, faint pink. The ml of titrating solution required is the number of "points" of free acid. If the solution is already pink after boiling, titrate with 0.1 N sulfuric acid instead to the permanent disappearance of the pink color. The number of ml of acid is then the points of free alkalinity.

Titrateable Metals

10 Place 20 grams or 20 ml of a homogenized lubricating solution sample into a 150-ml beaker, dilute with 20 ml deionized water and add 1 ml of concentrated HCl. Heat on a hot plate to separate the fatty acid layer. Cool and filter through Whatman #541 filter paper into a 200 ml tall form beaker. Cool, dilute to 100 ml in a glass-stoppered flask. Transfer a 25-ml aliquot from the glass-stoppered flask to a 200-ml tall form  
15 beaker. Add 1 drop of methyl red indicator solution and neutralize with NH<sub>4</sub>OH. Add 5 ml of "Reagent Solution 65", a 2 % by weight solution of hydroxylamine hydrochloride in water, and mix. Add 2 ml of "Reagent Solution 87", a solution of 8.7 % by weight of ammonium chloride, 57 % by weight concentrated aqueous ammonium hydroxide, and 0.5 % by weight magnesium EDTA in water, and mix. Add 2 ml of 10 % Sodium Cyanide solution and mix. Add about one-eighth teaspoon of "Indicator 24", a solid mixture of  
20 99.6 % by weight dextrose, 0.2 % by weight magnesium EDTA, and 0.2 % by weight Eriochrome black, and titrate with "Titrating Solution 86", a 0.4 % by weight solution of sodium EDTA in water, to a color change from a wine-red to a light blue, retaining the sample for the zinc titration.

25 
$$\% (Ca + Mg) = \frac{0.04(\text{ml of "Titrating Solution 86"})}{\text{original sample size}}$$

N.B.: If a sample contains iron and/or aluminum, a sharper end point is obtained if 10 ml of 30 % by weight triethanolamine in water is added to the sample prior to the addition of "Reagent Solution 87" in the calcium + magnesium determination.

30 Reset the buret to zero and add a few drops of "Reagent Solution 88", a solution of 18 % by weight formaldehyde and 2 % by weight methanol in water, to the sample from the calcium + magnesium titration and titrate with Titrating Solution 86 to a new red-to-blue end point. Add another drop of "Reagent Solution 88" and titrate with "Titrating Solution 86" again. Repeat until 1 drop of "Reagent Solution 88" requires no  
35 additional titration. The additional consumption of "Titrating Solution 86" represents zinc set free from the cyanide complex.

40 
$$\% Zn = \frac{0.0654(\text{ml added "Titrating Solution 86"})}{\text{original sample size}}$$

40 Pipet a 0.5-ml aliquot of the original filtered sample from its originally prepared 100-ml glass stoppered flask into a 100-ml glass-stoppered, graduated cylinder. Add 5 ml of "Reagent Solution 65", 10 ml of "Indicator 19", a solution of 1.5 % by weight of ammonium citrate and 0.05 % by weight of orthophenanthroline monohydrate in water, and 1.0 ml of "Reagent Solution 90", a solution of 5 % by weight of 1,10-phenanthroline in isopropyl alcohol. Dilute to 100 ml. Mix by upending twice and allow to stand for 1 hour.  
45 Then determine the percent transmittance at a wavelength of 510-525 nm. Read mg Fe from a standard curve. The standard curve is obtained by the following procedure: To a series of 100-ml glass-stoppered cylinders, add 0, 0.5, 1.0, 1.5, and 2.0 ml of "Standard Solution 91", a solution of 0.03 % by weight ferrous sulfate and 2 % by weight sulfuric acid in water. These amounts correspond to 0, 0.5, 0.1, 0.15, and 0.2 mg  
50 Fe. Then add 5 ml of "Reagent Solution 65" and 10 ml of "Indicator 19" to each cylinder. Dilute to 100 ml with deionized water and mix by upending twice. Allow to stand at least 10 minutes, then determine the percent transmittance of each standard, using a deionized water blank, at a wavelength of 510-525 nm (510 nm is preferred). Prepare a standard curve by plotting mg Fe against percent transmittance using semilogarithmic paper, with transmittance on the logarithmic scale and mg Fe on the arithmetic scale.

55 
$$\% Fe = \frac{0.1(\text{mg Fe from standard curve})}{\text{milliliters of original sample}}$$





**Table 1**  
**Characteristics of Experimental Lubricating Solutions**

Solution No.	Characteristic	Value:			
		For Experiment # 1 (No Additive)	For Experiment # 2 (EDTA Additive)	For Experiment # 3 (EDTA + PEG Additive)	For Experiment # 4 (EDTA + PEG Additive)
1	Soap Content, g/L	32			
	Free Acid Points	0			
	Viscosity, Sec.	14.5			
	Total Titratable Metals, weight %	0			
2	Soap Content, g/L	34	34	34	34
	Free Acid Points	0.4	0.4	0.4	0.4
	Viscosity, Sec.	14.5	16	16	16
	Total Titratable Metals, weight %	0.02	0	0	0
3	Soap Content, g/L	30	30	30	30
	Free Acid Points	0.3	0.3	0.3	0.3
	Viscosity, Sec.	14.5	15.5	14	14
	Total Titratable Metals, weight %	0.06	0	0	0
4	Soap Content, g/L	32	32	32	32
	Free Acid Points	0.4	0.4	0.4	0.4
	Viscosity, Sec.	14	16	14.5	14.5
	Total Titratable Metals, weight %	0.08	0	0	0
5	Soap Content, g/L	45	45	45	45
	Free Acid Points	0.2	0.2	0.2	0.2
	Viscosity, Sec.	0.18	0.103	0.095	0.095
	Total Titratable Metals, weight %				



Table 2:  
Coating Weight Results and Related Data

	Grams per Square Meter of:				Residual Conversion Coating	Ratio of:		Percent Reacted Lube in Total Lube
	Conversion Coating Loss	Nonreacted Lube	Reacted Lube	Total Lube		Reacted Lube to Conversion Coating Loss	Reacted Lube to Nonreacted Lube	
Exp. 1								
Sol. 1	2.60	4.34	10.51	14.85	8.25	4.0	2.4	70.7
Sol. 2	2.48	3.53	11.38	14.91	9.12	4.5	3.2	78.3
Sol. 3	1.48	2.71	4.48	7.20	10.31	3.0	1.7	62.4
Sol. 4	1.68	3.54	3.95	7.49	9.97	2.3	1.1	57.7
Exp. 2								
Sol. 2	2.48	3.36	11.84	15.20	9.50	4.8	3.5	77.9
Sol. 3	1.80	3.94	5.03	8.97	10.08	2.8	1.3	56.1
Sol. 4	2.24	8.01	4.82	12.93	9.32	2.2	0.6	38.2
Exp. 3								
Sol. 2	2.75	3.56	11.44	15.00	8.87	4.2	3.2	78.2
Sol. 3	2.02	3.03	9.10	12.13	9.86	4.5	3.0	76.0
Sol. 4	2.55	4.14	8.60	13.04	8.49	3.5	2.1	68.3
Exp. 4								
Original	1.86	4.82	2.60	7.42	17.53	1.4	0.5	35
1st Add.	2.07	4.28	6.97	11.25	17.27	3.4	1.6	62
2nd Add.	2.41	5.68	8.29	13.98	16.77	3.4	1.4	59
3rd Add.	3.51	5.91	9.23	15.14	15.07	2.6	1.6	60

The characteristics of the solutions after each of the additions in these experiments are also shown in Table 1. The results of the coating weight and related measurements from these experiments are shown in Table 2.

5 Experiment 1, a comparative example, shows that an increase in divalent metal cations decreases conversion coating loss and lube reactivity. The conversion coating loss goes from 2.6 down to 1.7 g/m<sup>2</sup> when the divalent metal increases to 0.08%. Along with this the reacted lube decreases from 10.5 down to 3.9 g/m<sup>2</sup>.

10 Experiment 2, also a comparative example, shows the effect the addition of EDTA tetrasodium salt has on the coating process. At all three levels of divalent metals, there is an increase in reacted lubricant. The biggest change is seen in solution #4 which contains the highest level of metal ions. The amount of nonreacted lube greatly increases, due to the increase in solution viscosity from 14 to 16 seconds.

Experiment 3, according to the present invention, shows how the polyethylene glycol not only returns the solution to a lower viscosity but also improves the ratio of reacted lube to nonreacted lube and of reacted lube to conversion coating loss. The nonreacted lube weights came down while the much more desirable reacted lube weights increased, even though the conversion coating loss stayed about the same.

15 Experiment 4, also according to the present invention, shows how the proper initial addition of EDTA tetrasodium salt and polyethylene glycol should preferably be based on the initial divalent metal ion concentration to optimize coating weights. The addition of large amounts of EDTA tetrasodium salt, as exemplified by the third addition in this experiment, will increase conversion coating loss but will not improve lube coating weights very much, once substantially all of the divalent metal cations present have been complexed. The second addition of complexing agent thus leaves this particular solution with more desirable lubricating properties overall than are produced by the third addition, even though the concentration of titratable metals remains well above 0.01 % by weight after the second addition but is below that after the third addition. Thus this third addition of EDTA brings the solution outside the most preferred range of complexing agent concentrations, even though still within the scope of the invention.

20 Although it is preferable, as already stated, to keep the concentration of titratable divalent metal ions in the solutions according to this invention below 0.05 weight %, the invention can be useful in solutions containing up to 0.2 weight % of such titratable divalent metal ions.

30

#### Claims

1. A liquid composition of matter, consisting essentially of: (A) water; (B) a reactive metallic soap component; (C) a complexing agent component; (D) an OSOC component consisting of organic molecules having at least one hydroxyl or ether oxygen atom for each eight carbon atoms and stable in solution or dispersion in the composition; and (E) up to about 0.2 % by weight titratable metals.

2. A composition according to claim 1, wherein the OSOC component is selected from molecules containing at least one hydroxyl or ether oxygen atom for every two carbon atoms.

3. A composition according to claim 2, wherein the complexing agent is selected from the group consisting of EDTA and its salts, NTA and its salts, NEDTA and its salts, diethylene triamine pentaacetic acid and its salts, diethanol glycine, and the material having CAS Registry No. 68611-02-8<sup>o</sup>.

4. A composition according to claim 1, wherein the complexing agent is selected from the group consisting of EDTA and its salts, NTA and its salts, NEDTA and its salts, diethylene triamine pentaacetic acid and its salts, diethanol glycine, and the material having CAS Registry No. 68611-02-9<sup>o</sup>.

5. A composition according to claim 4, wherein the OSOC component consists of molecules selected from the group consisting of alkylene glycols, poly(alkylene glycols), glycol ethers, ethoxylated alcohols, polymers and copolymers of ethylene oxide and propylene oxide, and glycerin.

6. A composition according to claim 1, wherein the OSOC component consists of molecules selected from the group consisting of alkylene glycols, poly(alkylene glycols), glycol ethers, ethoxylated alcohols, polymers and copolymers of ethylene oxide and propylene oxide, and glycerin.

7. A composition according to claim 6, wherein (i) the concentration of reactive soap is within the range of about 5 to about 150 g/L, (ii) the concentration of complexing agent component is not greater than an upper bound that is the greater of (A) about 0.1 g/L and (B) the minimum amount necessary to reduce the concentration of titratable metals in the composition below 0.05 % by weight, and (iii) the OSOC component consists essentially of PEG 4000 and its concentration in the composition is such as to produce a ratio between the concentration of the complexing agent component and the concentration of the OSOC component within the range between about 1 and about 5.

8. A composition according to claim 4, wherein (I) the concentration of reactive soap is within the range of about 5 to about 150 g/L, (II) the concentration of complexing agent component is not greater than an upper bound that is the greater of (A) about 0.1 g/L and (B) the minimum amount necessary to reduce the concentration of titratable metals in the composition below 0.05 % by weight, and (III) the OSOC component consists essentially of PEG 4000 and its concentration in the composition is such as to produce a ratio between the concentration of the complexing agent component and the concentration of the OSOC component within the range between about 1 and about 5.

9. A composition according to claim 8, wherein the complexing agent component is selected from EDTA and its salts.

10. A composition according to claim 7, wherein the complexing agent component is selected from EDTA and its salts.

11. In a process for phosphating a metal surface and subsequently contacting the phosphate layer formed thereby with an aqueous lubricating solution of a reactive lubricant component and a component of complexing agent for any divalent metal cations in said phosphate layer, under conditions so as to form a reacted lube layer on said metal surface, the improvement wherein said aqueous lubricating solution also contains a OSOC component consisting of organic molecules having at least one hydroxyl or ether oxygen atom for each eight carbon atoms.

12. A process according to claim 11, wherein the OSOC component of the lubricating solution is selected from molecules containing at least one hydroxyl or ether oxygen atom for every two carbon atoms.

13. A process according to claim 12, wherein the complexing agent in the lubricating solution is selected from the group consisting of EDTA and its salts, NTA and its salts, NEDTA and its salts, diethylene triamine pentaacetic acid and its salts, and diethanol glycine.

14. A process according to claim 11, wherein the OSOC component of the lubricating solution consists of molecules selected from the group consisting of alkylene glycols, poly(alkylene glycols), glycol ethers, ethoxylated alcohols, polymers and copolymers of ethylene oxide and propylene oxide, and glycerin.

15. A process according to claim 14, wherein, in the lubricating solution, (I) the concentration of reactive soap is within the range of about 5 to about 150 g/L, (II) the concentration of complexing agent component is not greater than an upper bound that is the greater of (A) about 0.1 g/L and (B) the minimum amount necessary to reduce the concentration of titratable metals in the composition below 0.05 % by weight, and (III) the OSOC component consists essentially of PEG 4000 and its concentration in the composition is such as to produce a ratio between the concentration of the complexing agent component and the concentration of the OSOC component within the range between about 1 and about 5.

16. A process according to claim 15, wherein the concentration of titratable metals in the lubricating solution is maintained below a preselected upper limit value during use of the solution for lubricating, by addition of complexing agent to the solution.

17. A process according to claim 14, wherein the concentration of titratable metals in the lubricating solution is maintained below a preselected upper limit value during use of the solution for lubricating, by addition of complexing agent to the solution.

18. A process according to claim 13, wherein the concentration of titratable metals in the lubricating solution is maintained below a preselected upper limit value during use of the solution for lubricating, by addition of complexing agent to the solution.

19. A process according to claim 11, wherein the concentration of titratable metals in the lubricating solution is maintained below a preselected upper limit value during use of the solution for lubricating, by addition of complexing agent to the solution.

20. A process according to claim 11, wherein the lubricating solution before beginning the process contains more than 0.05 % by weight of titratable metals, the concentration of titratable metals in the lubricating solution is reduced at the beginning of the process by adding to the lubricating solution an amount of complexing agent sufficient to provide a concentration of complexing agent in the solution that is within the range of about 5 to about 9 times the concentration of titratable metals that was present in the lubricating solution before beginning the process, and the concentration of titratable metals in the solution is maintained, during subsequent use of the solution for lubricating, within a range having an upper bound of about 0.05 % by weight and a lower bound of about two-thirds of the concentration of titratable metals after the first addition of complexing agent at the beginning of the process, by addition of more complexing agent to the solution as the solution is used.



European Patent  
Office

EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 90108988.8
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IN CI <sup>7</sup> )
X	<u>EP - A1 - 0 291 891</u> (NIHON PARKERIZINC CO.) * Claim 1; examples; page 3, lines 15-55 *	1-6, 11-14	C 23 C 22/12 C 23 C 22/28
X	<u>US - A - 4 728 373</u> (NAKAGAWA et al.) * Claim 1; examples; column 2, lines 5-16, 25-43 *	1-6, 11-14	
X	<u>US - A - 4 780 153</u> (GURDE et al.) * Claims 1, 2, 4-11, 13 *	1-6	
A	<u>US - A - 4 688 411</u> (HAGITA et al.) * Claim 1 *	1	
D, A	<u>US - A - 4 199 381</u> (NUSS et al.) * Claim 1 *	1	
			TECHNICAL FIELDS SEARCHED (IN CI <sup>7</sup> )  C 23 C 22/00 B 21 B 27/00 B 21 C 9/00
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
VIENNA		23-08-1990	PUSTERER
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EPO Form 900 (01/82)

## COMPOSITIONS AND PROCESSES FOR IMPROVED PREPARATION OF METALS FOR COLD FORMING

Field of the Invention

The present invention relates to compositions and methods for lubricating phosphated metal surfaces prior to drawing or other cold forming processes on the lubricated metal.

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Statement of Related Art

It has been known for many years to prepare metals for cold forming by phosphating followed by  
10 lubrication with a soap or similar material. Generally, phosphating from solutions that contain zinc ions, and sometimes also contain calcium, nickel, manganese, copper, and/or other divalent metal ions, is preferred as the phosphating step. An aqueous solution of alkali metal soap, capable of reacting with zinc phosphate to produce a very favorable form of zinc stearate called "reacted lube" in situ on the surface, is generally preferred for the lubrication stage.

15 Initially, a simple solution of reactive soap in water provides very effective lubrication. The lubrication process, however, is known to cause dissolution of part of the phosphate coating. For this and possibly other reasons, divalent metal ions accumulate in the lubricating solution as the process proceeds and eventually cause the lubricating coatings formed to become unsatisfactory.

U. S. Patent 4,199,381 of Apr. 22, 1980 to Nuss et al. teaches that, when lubricating surfaces formed in  
20 phosphating baths containing divalent metal ions that are incorporated into the phosphate coating formed, the results can be improved by incorporating complexing agents for such divalent ions into the lubricating solutions. The following sections of the specification of the Nuss patent, in so far as they are consistent with the statements made explicitly herein, are hereby incorporated into this specification by reference: Column 1 line 10 to column 2 line 4; column 2 lines 33 - 49; and column 3 lines 6 - 11.

25 Complexing agents as taught by Nuss are highly effective in increasing the useful life of lubricating solutions and in promoting usefully high coating weights of lubricant, but prolonged use of these complexing agents eventually results in increased lubricating solution viscosity, increased dissolution of the phosphate coating into the lubricating solution, drying problems, reduced lubricant adhesion, and higher proportions of less desirable "unreacted" lubricant in the lubricant coating formed. It is an object of the  
30 present invention further to improve the processes and compositions described by Nuss in order to ameliorate these difficulties.

U. S. Patent 3,556,996 of Jan. 19, 1971 to Jones et al. teaches the use of surfactants, including condensates of alcohols with ethylene oxide, in lubricating solutions, along with sugar and/or polyethylene glycol as optional components.

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Description of the Invention

In this description, except in the operating examples or where expressly stated to the contrary, all  
40 numbers describing amounts of materials or conditions of reaction or use are to be understood in all instances as modified by the word "about".

It has been found that large amounts of complexing agents can be harmful to the reactive lubrication process after phosphating, so that better results are obtained by observing an upper limit on the concentration of complexing agent present, the upper limit being connected with the amount of complex-  
45 able, divalent cations introduced into the lubricating solution during use. It has also been found that the reactive lubrication process can be improved by using aqueous lubricating solutions that, in addition to soluble metallic soaps having aliphatic anions with 8 to 22 carbon atoms and hydrolysis resistant complexing agents as taught by Nuss, contain water soluble or dispersible organic compounds that are stable in solution or dispersion under normal conditions of applying lubricant to phosphated surfaces and  
50 that contain at least one hydroxyl or ether oxygen for each eight carbon atoms. This latter component is referred to briefly hereinafter as "OSOC" (for "oxygenated soluble organic compound"). In the definition of the OSOC component, neither oxygen atom of a carboxyl or carboxylate group is considered to be an ether or hydroxyl oxygen. Preferably, the OSOC component molecules contain at least one hydroxyl or ether oxygen for each two carbon atoms.

art, including technical sodium stearate containing from 40 to 90 % of C<sub>18</sub> soaps, as used in some examples of the Nuss patent noted above, but technical mixtures including a higher proportion of sodium stearate are generally most highly preferred. The complexing agent similarly may be any material known as such in the art, but preferably is selected from the group consisting of ethylene diaminetetraacetic acid (hereinafter "EDTA") and its salts, nitrilotriacetic acid (hereinafter "NTA") and its salts, N-hydroxyethylethylene diaminetriacetic acid (hereinafter "NEDTA") and its salts, diethylene triamine pentaacetic acid and its salts, diethanol glycine, and a material having CAS Registry No. 68611-02-9\* and described by its manufacturer as "glycine,N,N'-1,2-ethanedylbis(N-carboxymethyl)-, reaction products with citric acid, D-gluconic acid, and triethanolamine, sodium salt." EDTA and its salts are most preferred.

The OSOC component is preferably selected from the group consisting of alkylene glycols, polyalkylene glycols, glycol ethers, ethoxylated alcohols, polymers and copolymers of ethylene oxide and propylene oxide, and glycerin.

For both the complexing agent and the OSOC component, mixtures of materials from the preferred group are equally as preferred as single chemical types of materials, unless otherwise noted.

Poly(ethylene glycol), hereinafter "PEG", is more preferred than other OSOC materials, with PEG having a molecular weight of about 4000, hereinafter "PEG 4000", being most preferred. When the OSOC component consists essentially of PEG 4000, it is preferred that the ratio of the concentration of the complexing agent to the concentration of the OSOC component lie within the range of 1 - 5, more preferably within the range of 2.5 to 3.5, and most preferably within the range of 2.9 - 3.1.

It is preferred that the concentration of reactive soap in the solutions according to the invention lie within the range of 5 to 150 g/L of solution. The preferable concentrations of complexing agent are determined by balancing several considerations, as noted further below.

A process embodiment of this invention may be performed by contacting a suitable phosphated surface with a lubricating solution according to the invention, as generally described above. It is believed that there is no advantage from the presence of the complexing agent in the very early stages of use of a freshly prepared lubricating solution, before any significant amounts of divalent metal ions have accumulated in the lubricating solution as a result of its exposure to a phosphated surface. However, it has been found that there is no apparent harm from an initial concentration of complexing agent as high as 0.1 gram per liter (hereinafter "g/L"), and the use of solutions initially made up to contain about this amount, or slightly less, of complexing agent is generally preferred in practice, in order to avoid the need to add complexing agent within a relatively short time after a fresh lubricating solution has been put into use.

An ideal lubricating process would maintain a consistent, high coating weight level of reacted lube, avoid the introduction into the lubricating solution of byproducts that interfere with the desired reaction between constituents of the phosphate coating and constituents of the lubricating solution, and remove little or none of the phosphate coating that was on the metal when it entered the lubricating solution. No actual lubricating solution known can accomplish such ideal lubrication, but preferable practical baths tend toward maximizing the ratio of reacted lube coating weight to conversion coating loss, with consideration toward optimizing the ratio of reacted lube coating weight to unreacted lube coating weight.

The most preferred embodiments of the process according to the invention utilize complexing agents and OSOC component in lubricating baths from near the beginning of use of a freshly made bath. In such embodiments, satisfactory operating conditions can generally be attained by selecting an upper bound on the concentration of "titratable metals", as defined exactly below, and by adding complexing agent after each measurement of titratable metals concentration that is higher than the selected upper limit. The amount of complexing agent should be at least sufficient to bring the concentration of titratable metals under a selected upper limit value. The best upper limit value may be determined most precisely from experience with each particular lubricating solution composition and type of base metal and phosphate coating lubricated, but in general an upper limit of 0.05 % by weight or less is preferred.

Most preferably, lubricating processes and solutions according to this invention should be controlled, from the beginning of use of a freshly made solution, so that the concentration of titratable metals never rises above its selected upper limit during the entire period of use of a lubricating solution according to the invention. Therefore, it is more preferable to add sufficient complexing agent, after each measurement of titratable metals, to bring the titratable metals concentration below two-thirds or less of its upper limit value immediately after addition, and to measure the titratable metals concentration sufficiently often so as to assure that the concentration never rises above the selected upper limit. It is generally most preferable in such situations to add sufficient complexing agent to bring the titratable metals concentration below 0.01 % by weight after each measurement of a higher value for this concentration.

While the method described above of utilizing lubricating solutions that contain complexing agent and OSOC components from at or near the beginning of their use is most preferred, the process according to

this invention may also be usefully embodied by starting with a conventional lubricating solution, containing little or no complexing agent, that has already been used for phosphating to a sufficient extent to accumulate a concentration of titratable metals greater than the desired upper limit for processes according to this invention. In such an embodiment, it has been found that it may be disadvantageous to add the very large amount of complexing agent that might be needed to reduce the concentration of titratable metals to very near zero. Such a large amount of complexing agent may cause excessive conversion coating losses during lubricating. Instead, when a process according to this invention is being initiated with a lubricating solution already containing more than 0.05 % by weight of titratable metals, it is preferable to add initially an amount of complexing agent that will produce a concentration of complexing agent in the solution that is within the range of 5 to 9 times the measured titratable metals concentration, with a ratio of 6.5 - 7.5 most preferred. At the same time, sufficient OSOC component to maintain the preferred ratio between the complexing agent and the OSOC component as stated above is also preferably added. The concentration of titratable metals remaining after this initial addition of complexing agent is then preferably measured; it will usually be between 0.01 and 0.05. After the initial addition of complexing agent, the process according to the invention is preferably continued in the same general manner as described above for embodiments in which complexing agent is added to the lubricating solution from the beginning of its use, except that the additions of complexing agent should be limited so that they do not reduce the concentration of titratable metals below three-quarters of their concentration after the initial addition of complexing agent.

In all processes according to this invention, the OSOC component preferably should be added to the lubricating solution at the same time as the complexing agent, in sufficient amount to maintain the ratio between these two components within the already stated preferred range.

After some operating experience with the same or a similar type of metal substrate and phosphating conditions, it is readily feasible to operate the process according to this invention successfully without explicitly measuring the concentrations of dissolved titratable metals, simply by adding appropriate amounts of complexing agent and OSOC components to a lubricating solution at intervals as the solution is used for lubricating.

The temperature of the lubricating solution and the time of contact between the lubricating solution and the phosphated surface in any process according to this invention are generally within the range of such conditions as used in the art for reactive lubrication. For example, the temperature is usually preferably between 70 and 90° C and the time of contact between 1 and 10 minutes.

The practice of the invention may be further appreciated with the help of the following non-limiting operating examples.

### Examples

#### General Conditions for All the Examples and Comparative Examples

The temperature of the lubricating solutions was maintained at 79° C, and phosphated metal specimens were contacted with the solution for 5 minutes, then dried for 15 minutes in an oven maintained at 121° C. The test specimens were Type 1010 cold rolled steel that had been phosphated by use of Bonderite® 181x, a commercial zinc phosphating solution available from the Parker + Amchem Division of Henkel Corporation, Madison Heights, Michigan, in a solution maintained with a total acid number of 30 points. (Points in this instance are defined as the number of milliliters of 0.1 N NaOH solution required to titrate a 5 ml sample of the phosphating solution to a phenolphthalein end point.) The average phosphate coating weight was 12.8 grams per square meter of surface (g/m<sup>2</sup>) for all the panels except those used in Experiment 5, for which the average coating weight was 21 g/m<sup>2</sup>.

The free acid or free alkalinity and the titratable metals content of the lubricating solutions were measured according to the following procedures:

#### Free Acid

Pour 200 ml of a solution of 0.2 % by weight phenolphthalein in isopropyl alcohol into a 400 ml beaker, then add a 10 ml sample of hot lubricating solution, measured with a conical graduate or a pipet. Heat the

mixture in the beaker to boiling, and boil for at least one minute. Remove from heat and titrate immediately, while the solution is still hot, with 0.1 N NaOH solution if the solution is clear rather than pink, to the development of a permanent, faint pink. The ml of titrating solution required is the number of "points" of free acid. If the solution is already pink after boiling, titrate with 0.1 N sulfuric acid instead to the permanent disappearance of the pink color. The number of ml of acid is then the points of free alkalinity.

#### Titrateable Metals

Place 20 grams or 20 ml of a homogenized lubricating solution sample into a 150-ml beaker, dilute with 20 ml deionized water and add 1 ml of concentrated HCl. Heat on a hot plate to separate the fatty acid layer. Cool and filter through Whatman #541 filter paper into a 200 ml tall form beaker. Cool, dilute to 100 ml in a glass-stoppered flask. Transfer a 25-ml aliquot from the glass-stoppered flask to a 200-ml tall form beaker. Add 1 drop of methyl red indicator solution and neutralize with  $\text{NH}_4\text{OH}$ . Add 5 ml of "Reagent Solution 65", a 2 % by weight solution of hydroxylamine hydrochloride in water, and mix. Add 2 ml of "Reagent Solution 87", a solution of 6.7 % by weight of ammonium chloride, 57 % by weight concentrated aqueous ammonium hydroxide, and 0.5 % by weight magnesium EDTA in water, and mix. Add 2 ml of 10 % Sodium Cyanide solution and mix. Add about one-eighth teaspoon of "Indicator 24", a solid mixture of 99.6 % by weight dextrose, 0.2 % by weight magnesium EDTA, and 0.2 % by weight Eriochrome black, and titrate with "Titrating Solution 86", a 0.4 % by weight solution of sodium EDTA in water, to a color change from a wine-red to a light blue, retaining the sample for the zinc titration.

$$\% \text{ (Ca + Mg)} = \frac{0.04(\text{ml of "Titrating Solution 86"})}{\text{original sample size}}$$

N.B.: If a sample contains iron and/or aluminum, a sharper end point is obtained if 10 ml of 30 % by weight triethanolamine in water is added to the sample prior to the addition of "Reagent Solution 87" in the calcium + magnesium determination.

Reset the buret to zero and add a few drops of "Reagent Solution 88", a solution of 18 % by weight formaldehyde and 2 % by weight methanol in water, to the sample from the calcium + magnesium titration and titrate with Titrating Solution 86 to a new red-to-blue end point. Add another drop of "Reagent Solution 88" and titrate with "Titrating Solution 86" again. Repeat until 1 drop of "Reagent Solution 88" requires no additional titration. The additional consumption of "Titrating Solution 86" represents zinc set free from the cyanide complex.

$$\% \text{ Zn} = \frac{0.0654(\text{ml added "Titrating Solution 86"})}{\text{original sample size}}$$

Pipet a 0.5-ml aliquot of the original filtered sample from its originally prepared 100-ml glass stoppered flask into a 100-ml glass-stoppered, graduated cylinder. Add 5 ml of "Reagent Solution 65", 10 ml of "Indicator 19", a solution of 1.5 % by weight of ammonium citrate and 0.05 % by weight of orthophenanthroline monohydrate in water, and 1.0 ml of "Reagent Solution 90", a solution of 5 % by weight of 1,10-phenanthroline in isopropyl alcohol. Dilute to 100 ml. Mix by upending twice and allow to stand for 1 hour. Then determine the percent transmittance at a wavelength of 510-525 nm. Read mg Fe from a standard curve. The standard curve is obtained by the following procedure: To a series of 100-ml glass-stoppered cylinders, add 0, 0.5, 1.0, 1.5, and 2.0 ml of "Standard Solution 91", a solution of 0.03 % by weight ferrous sulfate and 2 % by weight sulfuric acid in water. These amounts correspond to 0, 0.5, 0.1, 0.15, and 0.2 mg Fe. Then add 5 ml of "Reagent Solution 65" and 10 ml of "Indicator 19" to each cylinder. Dilute to 100 ml with deionized water and mix by upending twice. Allow to stand at least 10 minutes, then determine the percent transmittance of each standard, using a deionized water blank, at a wavelength of 510-525 nm (510 nm is preferred). Prepare a standard curve by plotting mg Fe against percent transmittance using semilogarithmic paper, with transmittance on the logarithmic scale and mg Fe on the arithmetic scale.

$$\% \text{ Fe} = \frac{0.1(\text{mg Fe from standard curve})}{\text{milliliters of original sample}}$$



The "titratable metals" concentration of the solution is then defined as: % Zn + (1.64)(% Ca + Mg) + (1.16)(% Fe).

The viscosity of the lubricating solutions was measured with a #2 Zahn Cup.

Coating weights and other related characteristics of the samples are defined and/or were determined as follows:

W1 = Weight (in grams) of panel and phosphate coating.

W2 = Weight (in grams) of panel, phosphate coating, and lube coating after exposure to lubricating solution.

W3 = Weight (in grams) of panel after exposure to phosphating and lubricating solutions, followed by water strip.

Water strip: Immerse panel in boiling deionized water, in sufficient volume to provide at least about 4.3 ml of water per square centimeter of panel surface, for three minutes. Remove panel and rinse by immersion in a similar volume of boiling deionized water for three minutes. Remove rinsed panel and dry in oven, cool to ambient temperature, and weigh.

W4 = Weight (in grams) of panel after exposure to phosphating and lubricating solutions, followed by water strip as above and solvent strip.

Solvent Strip: Place panel in extraction portion of a Soxhlet or similar extractor that accumulates freshly distilled solvent in a container to a specified level, then drains the accumulated solvent, and repeats the cycle. Make sure all panels loaded are completely covered when the container is filled to just below the level that produces drainage. Extract for at least 30 minutes with condensate from a vigorously refluxing mixture of 55 % by weight isopropyl alcohol, 32 % by weight n-heptane, and the balance 2-ethoxyethanol. Remove panel, dry in oven, cool to ambient temperature, and weigh.

W5 = Weight (in grams) of panel after exposure to phosphating and lubricating solutions, followed by water strip and solvent strip as specified above and then by chromic acid strip.

Chromic Acid Strip: Prepare solution by dissolving 800 g of CrO<sub>3</sub> in sufficient water to make 4 liters. Heat solution to 82° C and maintain at that temperature with stirring and thermostatic control. Immerse panel for 5 minutes. Remove panel from hot solution, rinse quickly in cold water, dry with clean compressed air, and weigh. Surface Area is measured in square meters.

Surface Area is measured in square meters.

$$A) \text{ Conversion coating loss} = \frac{(W1 - W4)}{\text{Surface Area}}$$

$$B) \text{ Nonreacted lube} = \frac{(W2 - W3)}{\text{Surface Area}}$$

$$C) \text{ Reacted lube} = \frac{(W3 - W4)}{\text{Surface Area}}$$

$$D) \text{ Residual Conversion coating} = \frac{(W4 - W5)}{\text{Surface Area}}$$

$$E) \text{ Total lube} = \text{Nonreacted lube} + \text{Reacted lube.}$$

#### Specific Experiments

An initial lubricating solution as freshly made up consisted of 3.6 % by weight in water of a sodium soap mixture that was made by neutralizing with sodium hydroxide a technical fatty acid mixture that is at least 95 % stearic acid. Solution No. 1 was this freshly made solution, while solutions Nos. 2 - 5 had been aged through actual use to lubricate phosphated surfaces. Characteristics of the solutions at the start are given in Table 1. The following experiments were then performed:

##### Experiment #1

Coated panels in solutions 1 - 4.

Measured coating weights.

##### Experiment #2

Added 1.5 g/L EDTA tetrasodium salt to Solution 2.

Added 4 g/L EDTA tetrasodium salt to Solution 3.

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Added 5.5 g/L EDTA tetrasodium salt to Solution 4. Coated panels in solutions 2 - 4 as modified by these first additions.

Measured coating weights.

### Experiment #3

5 Added 0.5 g/L of PEG 4000 to Solution 2.

Added 1.25 g/L of PEG 4000 to Solution 3.

Added 1.8 g/L of PEG 4000 to Solution 4.

Coated panels in solutions 2 - 4 as modified by these second additions.

Measured coating weights.

10 Experiment #4

Added various levels of EDTA tetrasodium salt (complexing salt) and PEG 4000 to solution 5, coating panels after each additions.

1st Addition: 5 g/L complexing salt, 2.5 g/L PEG.

2nd Addition: 5 g/L complexing salt, No PEG

15 3rd Addition: 5 g/L complexing salt, 2.5 g/L PEG

Totals Added: 15 g/L complexing salt, 5 g/L PEG.

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Table 1  
Characteristics of Experimental Lubricating Solutions

Solution No.	Characteristic	Value:			
		For Experiment # 1 (No Additive)	For Experiment # 2 (EDTA Additive)	For Experiment # 3 (EDTA + PEG Additive)	
1	Soap Content, g/L	32			
	Free Acid Points	0			
	Viscosity, Sec.	14.5			
	Total Titratable Metals, weight %	0			
2	Soap Content, g/L	34	34	34	
	Free Acid Points	0.4	0.4	0.4	
	Viscosity, Sec.	14.5	16	15	
	Total Titratable Metals, weight %	0.02	0	0	
3	Soap Content, g/L	30	30	30	
	Free Acid Points	0.3	0.3	0.3	
	Viscosity, Sec.	14.5	15.5	14	
	Total Titratable Metals, weight %	0.06	0	0	
4	Soap Content, g/L	32	32	32	
	Free Acid Points	0.4	0.4	0.4	
	Viscosity, Sec.	14	16	14.5	
	Total Titratable Metals, weight %	0.08	0	0	
Experiment # 4					
		At Start	After First Addition (EDTA + PEG)	After Second Addition (EDTA Only)	After Third Addition (EDTA + PEG)
5	Soap Content, g/L	45	45	45	45
	Free Acid Points	0.2	0.2	0.2	0.3
	Total Titratable Metals, weight %	0.18	0.103	0.035	0

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Table 2: Coating Weight Results and Related Data

	Grams per Square Meter of:				Ratio of:			
	Conversion Coating Loss	Nonreacted Lube	Reacted Lube	Total Lube	Residual Conversion Coating	Reacted Lube to Conversion Coating Loss	Reacted Lube to Nonreacted Lube	Percent Reacted Lube in Total Lube
<b>Exp. 1</b>								
Sol. 1	2.60	4.34	10.51	14.85	8.25	4.0	2.4	70.7
Sol. 2	2.48	3.53	11.38	14.91	9.12	4.5	3.2	76.3
Sol. 3	1.49	2.71	4.49	7.20	10.31	3.0	1.7	62.4
Sol. 4	1.69	3.54	3.95	7.49	9.97	2.3	1.1	57.7
<b>Exp. 2</b>								
Sol. 2	2.48	3.36	11.84	15.20	9.50	4.8	3.5	77.9
Sol. 3	1.80	3.94	5.03	8.97	10.09	2.8	1.3	56.1
Sol. 4	2.24	8.01	4.92	12.93	9.32	2.2	0.6	38.2
<b>Exp. 3</b>								
Sol. 2	2.75	3.56	11.44	15.00	8.87	4.2	3.2	76.2
Sol. 3	2.02	3.03	9.10	12.13	9.68	4.5	3.0	75.0
Sol. 4	2.55	4.14	8.90	13.04	8.49	3.5	2.1	68.3
<b>Exp. 4</b>								
Original	1.86	4.82	2.60	7.42	17.53	1.4	0.5	35
1st Add.	2.07	4.28	6.97	11.25	17.27	3.4	1.6	62
2nd Add.	2.41	5.69	8.29	13.98	16.77	3.4	1.4	59
3rd Add.	3.51	5.91	9.23	15.14	15.07	2.6	1.6	60

The characteristics of the solutions after each of the additions in these experiments are also shown in Table 1. The results of the coating weight and related measurements from these experiments are shown in Table 2.

5 Experiment 1, a comparative example, shows that an increase in divalent metal cations decreases conversion coating loss and lube reactivity. The conversion coating loss goes from 2.6 down to 1.7 g/m<sup>2</sup> when the divalent metal increases to 0.08%. Along with this the reacted lube decreases from 10.5 down to 3.9 g/m<sup>2</sup>.

10 Experiment 2, also a comparative example, shows the effect the addition of EDTA tetrasodium salt has on the coating process. At all three levels of divalent metals, there is an increase in reacted lubricant. The biggest change is seen in solution #4 which contains the highest level of metal ions. The amount of nonreacted lube greatly increases, due to the increase in solution viscosity from 14 to 16 seconds.

15 Experiment 3, according to the present invention, shows how the polyethylene glycol not only returns the solution to a lower viscosity but also improves the ratio of reacted lube to nonreacted lube and of reacted lube to conversion coating loss. The nonreacted lube weights came down while the much more desirable reacted lube weights increased, even though the conversion coating loss stayed about the same.

20 Experiment 4, also according to the present invention, shows how the proper initial addition of EDTA tetrasodium salt and polyethylene glycol should preferably be based on the initial divalent metal ion concentration to optimize coating weights. The addition of large amounts of EDTA tetrasodium salt, as exemplified by the third addition in this experiment, will increase conversion coating loss but will not improve lube coating weights very much, once substantially all of the divalent metal cations present have been complexed. The second addition of complexing agent thus leaves this particular solution with more desirable lubricating properties overall than are produced by the third addition, even though the concentration of titratable metals remains well above 0.01 % by weight after the second addition but is below that  
25 after the third addition. Thus this third addition of EDTA brings the solution outside the most preferred range of complexing agent concentrations, even though still within the scope of the invention.

Although it is preferable, as already stated, to keep the concentration of titratable divalent metal ions in the solutions according to this invention below 0.05 weight %, the invention can be useful in solutions containing up to 0.2 weight % of such titratable divalent metal ions.

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## Claims

35 1. A liquid composition of matter, consisting essentially of: (A) water; (B) a reactive metallic soap component; (C) a complexing agent component; (D) an OSOC component consisting of organic molecules having at least one hydroxyl or ether oxygen atom for each eight carbon atoms and stable in solution or dispersion in the composition; and (E) up to about 0.2 % by weight titratable metals.

2. A composition according to claim 1, wherein the OSOC component is selected from molecules containing at least one hydroxyl or ether oxygen atom for every two carbon atoms.

40 3. A composition according to claim 2, wherein the complexing agent is selected from the group consisting of EDTA and its salts, NTA and its salts, NEDTA and its salts, diethylene triamine pentaacetic acid and its salts, diethanol glycine, and the material having CAS Registry No. 68611-02-9\*.

45 4. A composition according to claim 1, wherein the complexing agent is selected from the group consisting of EDTA and its salts, NTA and its salts, NEDTA and its salts, diethylene triamine pentaacetic acid and its salts, diethanol glycine, and the material having CAS Registry No. 68611-02-9\*.

5. A composition according to claim 4, wherein the OSOC component consists of molecules selected from the group consisting of alkylene glycols, poly(alkylene glycols), glycol ethers, ethoxylated alcohols, polymers and copolymers of ethylene oxide and propylene oxide, and glycerin.

50 6. A composition according to claim 1, wherein the OSOC component consists of molecules selected from the group consisting of alkylene glycols, poly(alkylene glycols), glycol ethers, ethoxylated alcohols, polymers and copolymers of ethylene oxide and propylene oxide, and glycerin.

7. A composition according to claim 6, wherein (I) the concentration of reactive soap is within the range of about 5 to about 150 g/L, (II) the concentration of complexing agent component is not greater than an upper bound that is the greater of (A) about 0.1 g/L and (B) the minimum amount necessary to reduce the concentration of titratable metals in the composition below 0.05 % by weight, and (III) the OSOC component consists essentially of PEG 4000 and its concentration in the composition is such as to produce a ratio between the concentration of the complexing agent component and the concentration of the OSOC component within the range between about 1 and about 5.

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8. A composition according to claim 4, wherein (I) the concentration of reactive soap is within the range of about 5 to about 150 g/L, (II) the concentration of complexing agent component is not greater than an upper bound that is the greater of (A) about 0.1 g/L and (B) the minimum amount necessary to reduce the concentration of titratable metals in the composition below 0.05 % by weight, and (III) the OSOC component  
5 consists essentially of PEG 4000 and its concentration in the composition is such as to produce a ratio between the concentration of the complexing agent component and the concentration of the OSOC component within the range between about 1 and about 5.

9. A composition according to claim 8, wherein the complexing agent component is selected from EDTA and its salts.

10 10. A composition according to claim 7, wherein the complexing agent component is selected from EDTA and its salts.

11. In a process for phosphating a metal surface and subsequently contacting the phosphate layer formed thereby with an aqueous lubricating solution of a reactive lubricant component and a component of complexing agent for any divalent metal cations in said phosphate layer, under conditions so as to form a  
15 reacted lube layer on said metal surface, the improvement wherein said aqueous lubricating solution also contains a OSOC component consisting of organic molecules having at least one hydroxyl or ether oxygen atom for each eight carbon atoms.

12. A process according to claim 11, wherein the OSOC component of the lubricating solution is selected from molecules containing at least one hydroxyl or ether oxygen atom for every two carbon atoms.

20 13. A process according to claim 12, wherein the complexing agent in the lubricating solution is selected from the group consisting of EDTA and its salts, NTA and its salts, NEDTA and its salts, diethylene triamine pentaacetic acid and its salts, and diethanol glycine.

14. A process according to claim 11, wherein the OSOC component of the lubricating solution consists of molecules selected from the group consisting of alkylene glycols, poly(alkylene glycols), glycol ethers,  
25 ethoxylated alcohols, polymers and copolymers of ethylene oxide and propylene oxide, and glycerin.

15. A process according to claim 14, wherein, in the lubricating solution, (I) the concentration of reactive soap is within the range of about 5 to about 150 g/L, (II) the concentration of complexing agent component is not greater than an upper bound that is the greater of (A) about 0.1 g/L and (B) the minimum amount necessary to reduce the concentration of titratable metals in the composition below 0.05 % by weight, and  
30 (III) the OSOC component consists essentially of PEG 4000 and its concentration in the composition is such as to produce a ratio between the concentration of the complexing agent component and the concentration of the OSOC component within the range between about 1 and about 5.

16. A process according to claim 15, wherein the concentration of titratable metals in the lubricating solution is maintained below a preselected upper limit value during use of the solution for lubricating, by  
35 addition of complexing agent to the solution.

17. A process according to claim 14, wherein the concentration of titratable metals in the lubricating solution is maintained below a preselected upper limit value during use of the solution for lubricating, by addition of complexing agent to the solution.

18. A process according to claim 13, wherein the concentration of titratable metals in the lubricating  
40 solution is maintained below a preselected upper limit value during use of the solution for lubricating, by addition of complexing agent to the solution.

19. A process according to claim 11, wherein the concentration of titratable metals in the lubricating solution is maintained below a preselected upper limit value during use of the solution for lubricating, by addition of complexing agent to the solution.

45 20. A process according to claim 11, wherein the lubricating solution before beginning the process contains more than 0.05 % by weight of titratable metals, the concentration of titratable metals in the lubricating solution is reduced at the beginning of the process by adding to the lubricating solution an amount of complexing agent sufficient to provide a concentration of complexing agent in the solution that is within the range of about 5 to about 9 times the concentration of titratable metals that was present in the  
50 lubricating solution before beginning the process, and the concentration of titratable metals in the solution is maintained, during subsequent use of the solution for lubricating, within a range having an upper bound of about 0.05 % by weight and a lower bound of about two-thirds of the concentration of titratable metals after the first addition of complexing agent at the beginning of the process, by addition of more complexing agent to the solution as the solution is used.